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Patentanmeldung Nr. Patent application No. Demande de brevet n°

02358018.6

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For the President of the European Patent Office

Le Président de l'Office européen des brevets p.o.

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Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.
If no title is shown please refer to the description.
Si aucun titre n'est indiqué se referer à la description.)

Supported polymerisation catalysts

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SUPPORTED POLYMERISATION CATALYSTS

The present invention relates to supported catalysts suitable for the polymerisation of olefins and in particular to supported metallocene catalysts providing advantages for operation in gas phase processes.

In recent years there have been many advances in the production of polyolefin homopolymers and copolymers due to the introduction of metallocene catalysts. Metallocene catalysts offer the advantage of generally a higher activity than traditional Ziegler catalysts and are usually described as catalysts which are single site in nature. There have been developed several different families of metallocene complexes. In earlier years catalysts based on bis (cyclopentadienyl) metal complexes were developed, examples of which may be found in EP 129368 or EP 206794. More recently complexes having a single or mono cyclopentadienyl ring have been developed. Such complexes have been referred to as 'constrained geometry' complexes and examples of these complexes may be found in EP 416815 or EP 420436. In both of these complexes the metal atom eg. zirconium is in the highest oxidation state.

Other complexes however have been developed in which the metal atom may be in a reduced oxidation state. Examples of both the bis (cyclopentadienyl) and mono (cyclopentadienyl) complexes have been described in WO 96/04290 and WO 95/00526 respectively.

The above metallocene complexes are utilised for polymerisation in the presence of a cocatalyst or activator. Typically activators are aluminoxanes, in particular methyl aluminoxane or compounds based on boron compounds. Examples of the latter are borates such as trialkyl-substituted ammonium tetraphenyl- or tetrafluorophenyl-

borates. Catalyst systems incorporating such borate activators are described in EP 561479, EP 418044 and EP 551277.

The above metallocene complexes may be used for the polymerisation of olefins in solution, slurry or gas phase. When used in the gas phase the metallocene complex and/or the activator are suitably supported. Typical supports include inorganic oxides eg. silica or polymeric supports may alternatively be used.

Examples of the preparation of supported metallocene catalysts for the polymerisation of olefins may be found in WO 94/26793, WO 95/07939, WO 96/00245, WO 96/04318, WO 97/02297 and EP 642536.

WO 98/27119 describes supported catalyst components comprising ionic compounds comprising a cation and an anion in which the anion contains at least one substituent comprising a moiety having an active hydrogen. In this disclosure supported metallocene catalysts are exemplified in which the catalyst is prepared by treating the aforementioned ionic compound with a trialkylaluminium compound followed by subsequent treatment with the support and the metallocene.

WO 98/27119 also describes a method for activating a substantially inactive catalyst precursor comprising (a) an ionic compound comprising a cation and an anion containing at least one substituent comprising a moiety having an active hydrogen, (b) a transition metal compound and optionally, (c) a support by treatment with an organometallic compound thereby forming an active catalyst.

Various methods have been utilised to prepare supported catalysts of this type. For example WO 98/27119 describes several methods of preparing the supported catalysts disclosed therein in which the support is impregnated with the ionic compound. The volume of the ionic compound may correspond from 20 volume percent to greater than 200 volume percent of the total pore volume of the support. In a preferred preparative route the volume of the solution of the ionic compound does not exceed substantially, and is preferably equal to, the total pore volume of the support. Such methods of preparation may be referred to as incipient precipitation or incipient wetness techniques.

More recently WO 02/06357 describes an improved incipient wetness technique for the preparation of a supported metallocene catalyst system in which the support is impregnated with an ionic compound and the metallocene complex followed by

treatment with an organometallic compound.

We have now found an improvement in the incipient wetness technique which allows for reduced molar ratios of organometallic compound to the ionic compound resulting in better catalyst reproducibility and improved productivity in the gas phase as well as having economic benefits.

Thus according to the present invention there is provided a method for the preparation of a supported metallocene catalyst system said method comprising the steps of:

(i) mixing together in a suitable solvent

(a) an organometallic compound, and

(b) an ionic activator comprising a cation and an anion,

(ii) addition of the mixture from step (i) to a support material, and

(iii) addition of a metallocene complex in a suitable solvent,

characterised in that the molar ratio of organometallic compound (a) to ionic activator (b) in step (i) is less than 2.

Suitable solvents for use in the present invention include lower alkanes eg isohexane or aromatic solvents eg - toluene.

The preferred molar ratio of organometallic compound (a) to ionic activator (b) is less than 1 and most preferably in the range 0.3 to 0.8.

The preferred metal with respect to the organometallic compound is aluminium and the preferred metal for the ionic activator is boron whereby the molar ratio of Al/B is less than 2 and is preferably less than 1 and most preferably in the range 0.3 to 0.8.

The cation of the ionic compound may be selected from the group consisting of acidic cations, carbonium cations, silylium cations, oxonium cations, organometallic cations and cationic oxidizing agents.

Suitably preferred cations include trihydrocarbyl substituted ammonium cations eg. triethylammonium, tripropylammonium, tri(n-butyl)ammonium and similar. Also suitable are N.N-dialkylanilinium cations such as N,N-dimethylanilinium cations.

The preferred ionic activators are those wherein the cation of the ionic activator comprises a hydrocarbyl substituted ammonium salt and the anion comprises an aryl substituted borate..

Typical borates suitable as ionic activators include:

triethylammonium tetraphenylborate
triethylammonium tetraphenylborate,
tripropylammonium tetraphenylborate,
tri(n-butyl)ammonium tetraphenylborate,
tri(t-butyl)ammonium tetraphenylborate,
N,N-dimethylanilinium tetraphenylborate,
N,N-diethylanilinium tetraphenylborate,
trimethylammonium tetrakis(pentafluorophenyl) borate,
triethylammonium tetrakis(pentafluorophenyl) borate,
tripropylammonium tetrakis(pentafluorophenyl) borate,
tri(n-butyl)ammonium tetrakis(pentafluorophenyl) borate,
N,N-dimethylanilinium tetrakis(pentafluorophenyl) borate,
N,N-diethylanilinium tetrakis(pentafluorphenyl) borate.

A preferred type of activator suitable for use with the metallocene complexes of the present invention comprise ionic compounds comprising a cation and an anion wherein the anion has at least one substituent comprising a moiety having an active hydrogen.

Suitable activators of this type are described in WO 98/27119 the relevant portions of which are incorporated herein by reference.

Particular preferred activators of this type are alkylammonium tris(pentafluorophenyl) 4-(hydroxyphenyl) borates. A particularly preferred activator is bis(hydrogenated tallow alkyl) methyl ammonium tris (pentafluorophenyl) (4-hydroxyphenyl) borate.

With respect to this preferred type of ionic activator, the reaction product of an alkylammonium tris(pentaflurophenyl)-4-(hydroxyphenyl) borate and an organometallic compound, for example triethylaluminium, represents the product obtained from the aforementioned step (i).

The organometallic compound utilised in step (i) is typically chosen from those containing a metal of Groups 1- 14 of the Periodic Table but preferred organometallic compounds are those of Group 13 for example those containing aluminium.

Particularly preferred organometallic compounds are organoaluminium compounds for example trialkylaluminium compounds such as trimethylaluminium,

triethylaluminium or triisobutylaluminium.

The use of triisobutylaluminium as organometallic compound has been found to lead to improved product properties in the resultant polymers, in particular improved melt strength may be achieved.

Suitable support materials include inorganic metal oxides or alternatively polymeric supports may be used.

The most preferred support material for use with the supported catalysts according to the process of the present invention is silica. Suitable silicas include Crosfield ES70 and Davison 948 silicas.

The support material may be subjected to a heat treatment and/or chemical treatment to reduce the water content or the hydroxyl content of the support material. Typically chemical dehydration agents are reactive metal hydrides, aluminium alkyls and halides. Prior to its use the support material may be subjected to treatment at $100^{o}C$ to $1000^{o}C$ and preferably at 200 to $850^{o}C$ in an inert atmosphere under reduced pressure.

The support material may be further combined with an organometallic compound preferably an organoaluminium compound and most preferably a trialkylaluminium compound in a dilute solvent.

The support material is pretreated with the organometallic compound at a temperature of $-20^{o}C$ to $150^{o}C$ and preferably at $20^{o}C$ to $100^{o}C$.

Alternative supports for the present invention are non-porous polystyrenes for example divinylbenzene crosslinked polystyrene.

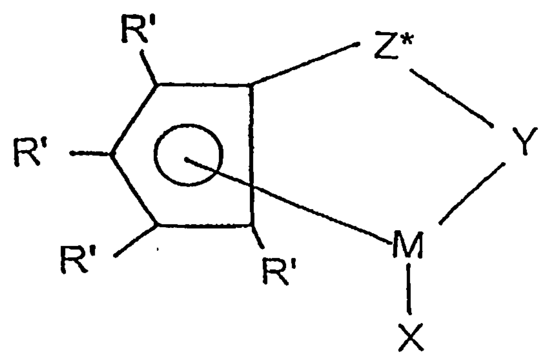
The metallocene complex may comprise for example a traditional bis(cyclopentadienyl) metallocene complex or more preferably a monocyclopentadienyl complex having a 'constrained geometry' configuration.

Bis(cyclopentadienyl) metallocene complexes may be represented by those disclosed in EP 129368 or EP 206794. Such complexes may be unbridged eg. bis(cyclopentadienyl) zirconium dichloride or bridged eg. ethylene bis(indenyl) zirconium dichloride. Other suitable metallocene complexes are those bis(cyclopentadienyl) diene complexes described in WO 96/04290.

Examples of moncyclopentadienyl complexes suitable for use in the present invention are described in EP 416815, EP 418044, EP 420436 and EP 551277.

Particularly suitable monocyclopentadienyl complexes are those disclosed in WO 95/00526 the disclosure of which is incorporated herein by reference.

Preferred metallocene complexes for use in the preparation of the supported catalysts of the present invention may be represented by the general formula:



wherein:-

R' each occurrence is independently selected from hydrogen, hydrocarbyl, silyl, germyl, halo, cyano, and combinations thereof, said R' having up to 20 nonhydrogen atoms, and optionally, two R' groups (where R' is not hydrogen, halo or cyano) together form a divalent derivative thereof connected to adjacent positions of the cyclopentadienyl ring to form a fused ring structure;

X is a neutral η^4 bonded diene group having up to 30 non-hydrogen atoms, which forms a π complex with M;

Y is -O-, -S-, -NR*-, -PR*-,

M is titanium or zirconium in the + 2 formal oxidation state;

Z* is SiR^*_2, CR^*_2, $SiR^*_2SIR^*_2$, $CR^*_2CR^*_2$, $CR^*=CR^*$, $CR^*_2SIR^*_2$, or GeR^*_2, wherein:

R* each occurrence is independently hydrogen, or a member selected from hydrocarbyl, silyl, halogenated alkyl, halogenated aryl, and combinations thereof, said R* having up to 10 non-hydrogen atoms, and optionally, two R* groups from Z* (when R* is not hydrogen), or an R* group from Z* and an R* group from Y form a ring system.

Examples of suitable X groups include s-trans-η^4-1,4-diphenyl-1,3-butadiene, s-trans-η^4-3-methyl-1,3-pentadiene; s-trans-η^4-2,4-hexadiene; s-trans-η^4-1,3-pentadiene; s-trans-η^4-1,4-ditolyl-1,3-butadiene; s-trans-η^4-1,4-bis(trimethylsilyl)-1,3-butadiene; s-cis-η^4-3-methyl-1,3-pentadiene; s-cis-η^4-1,4-dibenzyl-1,3-butadiene; s-cis-η^4-1,3-pentadiene; s-cis-η^4-1,4-bis(trimethylsilyl)-1,3-butadiene, said s-cis diene group forming a π-complex as defined herein with the metal.

Most preferably R' is hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, benzyl, or phenyl or 2 R' groups (except hydrogen) are linked together, the entire $C_5R'_4$ group thereby being , for example, an indenyl, tetrahydroindenyl, fluorenyl, terahydrofluorenyl, or octahydrofluorenyl group.

Highly preferred Y groups are nitrogen or phosporhus containing groups containing a group corresponding to the formula -N(R$''$)- or -P(R$''$)- wherein R$''$ is C_{1-10} hydrocarbyl.

Most preferred complexes are amidosilane - or amidoalkanediyl complexes.

Most preferred complexes are those wherein M is titanium.

Specific complexes suitable for use in the preparation of the supported catalysts of the present invention are those disclosed in the aforementioned WO 95/00526 and are incorporated herein by reference.

A particularly preferred complex for use in the preparation of the supported catalysts of the present invention is (t-butylamido) (tetramethyl-η^5-cyclopentadienyl) dimethyl silanetitanium -η^4-1.3 -pentadiene.

The molar ratio of metallocene complex to ionic activator employed in the method of the present invention may be in the range 1:10000 to 100:1. A preferred range is from 1:5000 to 10:1 and most preferred from 1:10 to 10:1.

It is advantageous in the present invention that the ionic activator is dried before contact with the organometallic compound. This enables lower ratios of organometallic compound to activator to be used without any detrimental effects on activity.

The supported metallocene catalysts of the present invention are most suitable for operation in the gas phase. Gas phase processes for the polymerisation of olefins , especially for the homopolymerisation and the copolymerisation of ethylene and α-olefins for example 1-butene, 1-hexene, 4-methyl-1-pentene are well known in the art. Particularly preferred gas phase processes are those operating in a fluidised bed.

Examples of such processes are described in EP 89691 and EP 699213 the latter being a particularly preferred process for use with the supported catalysts of the present invention.

Particularly preferred polymerisation processes are those comprising the polymerisation of ethylene or the copolymerisation of ethylene and α-olefins having from 3 to 10 carbon atoms.

Thus according to another aspect of the present invention there is provided a process for the polymerisation of ethylene or the copolymerisation of ethylene and α-olefins having from 3 to 10 carbon atoms, said process performed under polymerisation conditions in the present of a supported metallocene catalyst system prepared as hereinbefore described.

By use of the reduced molar ratio of the organometallic compound to the ionic activator in step (i) better reproducibilty of the catalyst may be achieved as well as higher activities. In addition polymer properties may be improved for example higher melt strength resulting in better product performance.

The present invention will now be further illustrated with reference to the following examples:

<u>Abbreviations</u>

TEA	triethylaluminium
TiBA	triisobutylaluminium
Ionic Activator A	$[N(H)Me(C_{18-22}H_{37-45})_2][B(C_6F_5)_3(C_6H_4OH)]$
Complex A	$(C_5Me_4SiMe_2N^tBu)Ti(\eta^4$-1,3-pentadiene)

<u>Example 1</u>

<u>Passivation of silica</u>

To a suspension of 60 g of silica Sylpol 948, previously calcined at 250°C for 5 hours under nitrogen, in 600 ml of essence was added 122.5 ml of an hexane solution of triethylaluminium (TEA) (0.98 mol/l). After two hours at 30°C the liquid phase was decanted and then silica was washed 5 times with 500 ml of essence and then dried at 60°C under vacuum. The aluminium content was 1.44 mmol/g support.

<u>Drying of the ionic activator A solution</u>

A solution of the ionic activator A in toluene (10.66 % wt) was dried by prolonged contact (1 week) with molecular sieve-4A (25% wt/wt) which had previously

been dried at 250°C for 2 days and cooled to ambient temperature under nitrogen atmosphere.

<u>Catalyst preparation</u>

1.54 ml of the above solution of the dried ionic activator A was reacted with 0.25 ml TEA in toluene (0.25 mol/l) (molar ratio Al/B=0.5). 4g of the passivated silica was slowly impregnated (15 min) with this solution and manually agitated until no lumps were visible followed by 30 min holding. 0.70 ml of a solution of the Complex A in heptane (9.17 % wt) was then slowly added (15 min) and manually agitated until no lumps were visible followed by 30 min holding. 11 ml of TEA solution in essence (5 mmol/l) was then added and the suspension was stirred for 15 minutes. The resultant catalyst was washed 3 times with 35 ml of essence and then dried under vacuum to give a loading of [Ti] = 29 μmol/g; [Al]=1.33 mmol/g

<u>Polymerisation data</u>

<u>Run conditions</u>

400 g of PE pellets as bed

T = 70°C

PC2= 6.5Bars.

C6/C2 (pressure ratio) constant at $26 10^{-4}$

SiO2/TEA impregnated used as scavenger.

H2 added during the gas phase composition (50 ml).

Polymerisation time = 60min

Quantity of catalyst injected = 0.1 g

At the end of the polymerisation reaction, polymer produced separated from polymer bed by simple sieving.

Activity: 105 g/ghbar

Density: 0.918 g/ml

MI (2.16)=0.75 g/10 min

<u>Example 2</u>

<u>Passivation of silica</u>

To a suspension of 20 g of silica Sylpol 948, previously calcined at 250°C for 5 hours under nitrogen, in 100 ml of essence was carefully added 42 ml of an hexane solution of triisobutylaluminium (TiBA) (0.952 mol/l) over 20 minutes. After two hours

at 30°C the liquid phase was decanted and the silica was washed 5 times with 500 ml of essence and then dried at 60°C under vacuum. The aluminium content was 1.05 mmol/g support.

Drying of the ionic activator A solution

A solution of the ionic activator A in toluene (10.66 % wt) was dried by prolonged contact (1 week) with molecular sieve-4A (25% wt/wt), which had previously been dried at 250°C for 2 days and cooled to ambient temperature under nitrogen atmosphere

Catalyst preparation

1.16 ml of the above dried ionic activator solution A was reacted with 0.19 ml TiBA solution in toluene (0.25 mol/l) (molar ratio Al/B=0.5). 3g of the passivated silica was slowly impregnated (15 min) with this solution and manually agitated until no lumps were visible followed by 30 min holding. 0.53 ml of a solution of the Complex A in heptane (9.17 % wt) was then slowly added (15 min) and manually agitated until no lumps were visible, followed by 30 min holding. 8.09 ml of TEA solution in essence (5 mmol/l) was the added and the suspension was stirred for 15 minutes. The catalyst was washed 3 times with 25 ml of essence then dried under vacuum to give a loading of [Ti] = 21 μmol/g of catalyst; [Al]=1.1 mmol/g.

Polymerisation data

Run conditions

400 g of PE pellets as bed

T = 70°C

PC2= 6.5Bars.

C6/C2 (pressure ratio) constant at 2610^{-4}

SiO2/TEA impregnated used as scavenger.

H2 added during the gas phase composition (50 ml).

Polymerisation time = 60min

Quantity of catalyst injected = 0.1 g

At the end of the polymerisation reaction, polymer produced separated from polymer bed by simple sieving.

Activity: 66 g/ghbar (3160 g/mmolhb)

Density: 0.9195 g/ml

MI (2.16)=1.05 g/10 min

MI (21.6)=24.5 g/10 min

MFR= 23.3

Melt strength (MS) measurements:

at 16 MPa: 5.54 cN

$\delta(MS)/\delta(P)$= 0.278 cN/MPa

Claims:

1. A process for the preparation of a supported metallocene catalyst system said method comprising the steps of:

(i) mixing together in a suitable solvent

(a) an organometallic compound, and

(b) an ionic activator comprising a cation and an anion,

(ii) addition of the mixture from step (i) to a support material, and

(iii) addition of a metallocene complex in a suitable solvent,

characterised in that the molar ratio of organometallic compound (a) to ionic activator (b) in step (i) is less than 2.

ABSTRACT

SUPPORTED POLYMERISATION CATALYSTS

A novel process for the preparation of a supported metallocene catalyst system said method comprises the steps of:

(i) mixing together in a suitable solvent

(a) an organometallic compound, and

(b) an ionic activator comprising a cation and an anion,

(ii) addition of the mixture from step (i) to a support material, and

(iii) addition of a metallocene complex in a suitable solvent,

characterised in that the molar ratio of organometallic compound (a) to ionic activator (b) in step (i) is less than 2.

By use of the reduced molar ratio of the organometallic compound to the ionic activator in step (i) better reproducibilty of the catalyst may be achieved as well as higher activities. In addition polymer properties may be improved for example higher melt strength resulting in better product performance.